Supporting Information for:

Near-Ideal Photodiodes from Sintered Gold Nanoparticle Films on Methyl-Terminated Si(111) Surfaces

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S1. Synthesis and Characterization of Au Nanoparticles

Butanethiol-capped Au nanoparticles were synthesized as described by Brust et al.[1] Unless noted, all chemicals were used as received. Briefly, 0.8025 g of $HAuCl_4 \cdot 3H_2O$ (Aldrich) was dissolved in 50 mL of stirred water. To this solution was added a 50 ml solution of toluene containing 4.56 g of a phase transfer reagent, $(C_8H_{17})_4NBr$ (Aldrich). All water was obtained from a Barnsted Nanopure system which purified water to a resistivity of 18 MΩ cm. The resulting biphasic mixture was then stirred vigorously. After 2 min, a solution containing one equivalent of butanethiol in 2 mL of toluene was added. A solution of 0.787 g $NaBH_4$ (Aldrich) dissolved in 50 mL of water was added drop-wise to the stirred biphasic solution over 5 min. During the addition of $NaBH_4$, the mixture turned dark purple, becoming nearly opaque. The solution was then capped and stirred for 12 h. The organic phase was then decanted away from the aqueous phase, transferred to a separatory funnel, and rinsed three times with 100 mL of water. The organic phase was then concentrated by rotary evaporation to 5 mL, and added dropwise into 1000 mL of cold ethanol. After settling overnight at 10 °C, the clear supernatant was decanted off and the precipitated Au nanoparticles were collected by centrifugation. The cleaned product was re-dissolved in 40 ml of dichloromethane, and either stored or used immediately. Au nanoparticles prepared by this protocol were routinely observed to have diameters between 4-6 nm, as measured by dynamic light scattering (PDExpert Light Scattering Workstation, Precision Detectors, Inc.).

S2. Chemical Modification of Si(111)

Si samples were obtained from several different vendors, but all n-Si wafers used to make Si/Au devices were (111)-oriented (± 0.5°) and were doped with phosphorous. n-Si wafers with nominal resistivities of 0.2, 3, and 60 Ω cm, were purchased from IWS, Virginia Semiconductor Inc., and Silicon Quest International, respectively. These wafers were single-side polished, single-side polished, and double-side polished, respectively, with thicknesses of 440, 550, and 390 ± 10 μm, respectively. For a given resistivity, each set of samples was made from a single wafer. Dopant densities for each wafer used were assessed from reference data[2] and current-voltage plots acquired with a standard 4 point-probe apparatus (Jandel Engineering Ltd.).

Prior to chemical modification, all Si surfaces were first degreased by sequential rinses with water, methanol (Aldrich), acetone (Aldrich), 1,1,1-trichloroethane (Aldrich), dichloromethane (Aldrich), 1,1,1-trichloroethane, acetone, methanol, and water. Samples were then dried under a stream of N_2(g) and immersed in an aqueous 3:1 (v/v) solution of conc. H_2SO_4 (Fisher) and H_2O_2 (30 % v/v, Fisher). The immersed samples were then heated at ~60 °C for at least 1 h, cooled, rinsed with water, and then used for chemical modification.

H-terminated Si(111) surfaces were obtained through wet chemical etching for 10 min in 11 M NH_4F (aq) (40% wt/wt, Transene). The samples were agitated periodically to minimize the formation of etch pits. Following etching, the monohydride-terminated surfaces were rinsed with flowing H_2O, dried under a stream of N_2(g), and immediately contacted with Au or further modified with CH_3– groups. Si samples were CH_3–terminated using a two-step chlorination/alkylation protocol. First, freshly etched Si(111) surfaces were transferred into a flush box and immersed in a saturated PCl_5 (Fluka)

solution in chlorobenzene (Aldrich) for 50 min at 90 ± 10 °C under an atmosphere of dry N_2(g) to convert the surficial Si-H groups into Si-Cl moieties. The chlorinated samples were then rinsed sequentially with chlorobenzene and tetrahydrofuran (THF, Aldrich) and dried under a stream of N_2(g). The samples were subsequently immersed for 8 h at 70 ± 10 °C in a THF solution of 1 M CH_3-MgCl (Aldrich). The silicon substrates were then rinsed with flowing THF, followed by a rinse with methanol, and then were immersed in methanol. The CH_3-terminated Si samples were then transported out of the flush box and further rinsed with methanol, followed by sonication sequentially in fresh methanol, acetone, methanol, and water. Finally, the Si substrates were dried under a stream of N_2(g) and were stored in dry test tubes under ambient conditions until used for device preparation.

S3. Preparation of n-Si(111)/Au Schottky Devices

Chemically modified n-Si(111) substrates were first cut into 5 cm x 1 cm strips and placed onto glass microscope slides.

n-Si(111)/Au Evaporated Devices For evaporated Au films, a similarly sized, thin (~200 μm thick) stainless-steel plate with regularly spaced holes (area = 0.2 cm^2) was centered on top of the Si strip. The samples were then loaded into a diffusion-pumped high-vacuum evaporation chamber (Vacuum Coating Unit Type LCI-14B, Consolidated Vacuum Corp.) and the chamber was evacuated to, and maintained at, a pressure of ≤ 4 x 10^{-5} torr. Approximately 30 nm of Au (99.99%wt, Alpha Aesar), as indicated by a quartz crystal oscillator thickness monitor (TM-100, R.D. Mathis), was thermally evaporated onto the exposed substrates at a rate of ≤ 0.2 nm s^{-1} from a tungsten

filament (R.D. Mathis) positioned 12 cm directly above the samples. Upon cooling, the samples were removed from the evaporation chamber. Strips of black vinyl electrical tape (Super 33+, 3M) with 0.2 cm^2 circular cutouts were placed on top of the Si, leaving the Si/Au spot exposed but masking the rest of the Si substrate. The Si strip was then diced further into 1 cm x 0.5 cm pieces, each having only 1 full Si/Au contact in the center. The backsides of these devices were etched with 49 wt % HF(aq) for up to 10 min, rinsed with water, and then rubbed with a In:Ga eutectic. The devices were then taped to a 5 cm x 1 cm stainless-steel strip. Ohmic contact to the top Au layer was made by spotting with silver paint (Silver Print II, GC Electronics).

n-Si(111)/Au NP Devices A strip of black vinyl electrical tape (Super 33+, 3M) with 0.2 cm^2 circular cutouts was placed on top of each Si strip, affixing each Si piece to an individual glass slide and exposing 6-7 circular regions on the Si. Concentrated Au suspensions in dichloromethane were then cast on top of the Si and supporting glass slide. Spray casting, rather than drop casting, of the Au suspension resulted in a more consistent and uniform Au NP film. An airbrush (CM-C Plus, Iwata Inc.) connected to filtered laboratory air, pressurized between 0.75 and 1 atm, was used for spray deposition. Following spraying, the Si substrates (still taped to the glass slides) were placed into a glass chamber connected to a Schlenk line. The chamber was evacuated to a pressure of 100 mtorr and backfilled with Ar. After three total pump-backfill repetitions, the samples were kept under vacuum and heated to 230 °C for approximately 30 min. During the heating, the Au NP film changed from wine-red color to metallic gold. After heating, the Si strips were cut free of the glass slides and diced further into pieces approximately 1 cm x 0.5 cm in dimensions, with each new fraction

containing a single 0.2 cm^2 Si/Au junction. Ohmic contact to the backside of the n-Si and the top Au film was then made as described above.

S4. Morphology of Au Films

The morphologies of the continuous, conductive Au thin films on Si were assessed via scanning electron microscopy (SEM). Electron micrographs were obtained using a LEO1550 VP Field Emission Scanning Electron Microscope (SEM) operating at 10 kV with an InLens Detector (30 μm aperture). Film images were obtained on films that had been deposited on 0.2 Ω cm resistivity, n-type Si(111) substrates. Figure S1 highlights representative top-down views of the film morphologies for the two types of studied Au films. The sintered Au NP films were noticeably uneven and clustered, with large (< 10^2 nm) grains. In contrast, the evaporated Au films were smoother with fewer grains, although the films possessed sporadic empty pockets/voids.

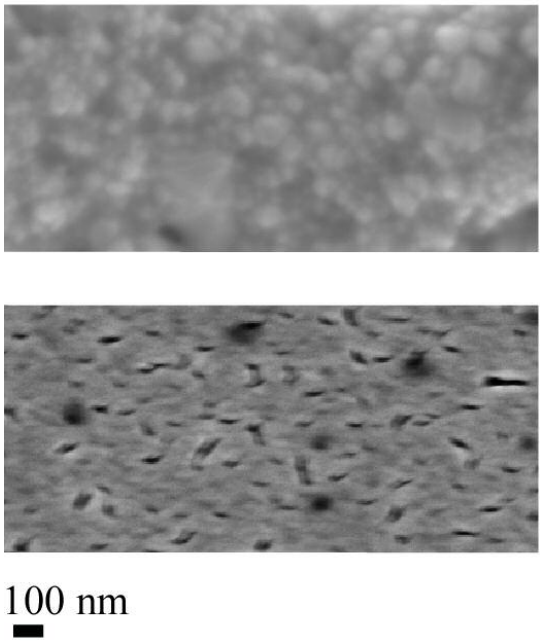

Figure S1. Representative scanning electron micrographs of a (top) sintered Au NP film and (b) thermally evaporated Au film on Si(111).

S5. *J-V* Data Collection

J-V data were obtained at a scan rate of 0.030 V s^{-1} and at a sampling of 1 mV per data point, with a Solartron Model 1287 potentiostat controlled by CorrWare software. Measurements were conducted with the silicon substrate as the working electrode and the top metal overlayer as the counter/reference electrode. For *J-V* data collected under uniform illumination, a tungsten-halogen lamp with a collimator and a frosted glass diffuser was used. The separation between the sample and the light source was adjusted slightly for each device, to maintain J_{sc} = 10 mA cm^{-2}. V_{oc} values are reported for a given J_{sc} value rather than energy conversion efficiencies at an absolute light intensity because the reflectivity losses of the Au films were not quantitatively assessed for both the evaporated and sintered NP devices.[3]

S6. Photoconductivity Decay Measurements

Long bulk lifetime, float-zone-grown Si(111) wafers were obtained from Cemat Silicon SA. The wafers were double-side polished with a thickness of 490 μm and a resistivity of 4000-6000 ohm cm. The wafers were diced into 2 cm x 2 cm squares and then chemically modified as described in S2. For CH_3-terminated Si(111) samples, substrates were additionally treated by soaking in a concentrated (~20 mg mL^{-1}) Au nanoparticle suspension in dichloromethane for 30 min. These samples were removed from the suspension without rinsing, and were used immediately for photoconductivity decay measurements. These same samples were heated under vacuum at 230 °C as described in S3, and were then used again for photoconductivity decay measurements.

Transient photoconductivity measurements of the Si samples following pulsed light excitation were made with a contactless radio-frequency (rf) system, as described elsewhere.[4,5] Briefly, Si samples were placed on top of a copper coil in an inductor-capacitor (*LC*) circuit having an approximate resonant frequency of 500 MHz. The output of a function generator (SMY01, Rohde & Schwarz) operating at the precise resonant frequency of the *LC* circuit was sent to a power splitter. One signal served as the reference rf signal and was sent to a phase-shifter (847-LTL, General Radio), which shifted the phase of the signal by 180°, and then sent into the reference input of a double-balanced frequency mixer (ZAY-2, Mini Circuits). The other signal coming out of the power splitter was amplified and sent through a directional coupler (CR-200-500, Merrimac), which then output the sum of the original rf signal and the reflected rf signal from the *LC* circuit. This summed signal was amplified and sent into the second input of the double-balanced frequency mixer. The output from the double-balanced frequency mixer was the sum phase signal of the reference and reflected signals. This summed phase signal was fed into a digital oscilloscope (TDS-210, Tektronix) and recorded. The time-dependent change in the summed rf output of the double-balanced frequency mixer was directly proportional to the transient change in conductivity of the Si sample following pulsed light excitation.

The transient photoconductivity decays were fit to a single exponential decay function, to obtain a photo-excited charge carrier lifetime, τ. From these lifetimes, an estimate of the surface charge-carrier recombination velocity was obtained from eq (S1),

$$S = \frac{d}{2}\left(\frac{1}{\tau} - \frac{1}{\tau_b}\right) \approx \frac{d}{2}\frac{1}{\tau} \qquad \text{(S1)}$$

where d is the Si sample thickness in cm, τ is the measured lifetime in s, and τ_b is the lifetime in s associated with bulk-recombination. For float-zone-grown Si, τ_b is large, so S and τ are approximately inversely proportional to each other. This approximation results in conservative estimates of S, as finite values of τ_b result in decreased overall values of S.

For long-lifetime samples, i.e. CH_3-terminated Si, 50 μs pulses of 828.7 ± 0.6 nm light from a diode laser (EAP Systems, Coherent) were used. For Si(111) etched in 40 wt % NH_4F(aq), the observed lifetimes were much shorter, requiring 50 ns pulses of 905 ± 7 nm light from a SPL 90_3 diode laser (OSRAM) with an ETX 10-A driver (EODevices). For either type of excitation, the incident power density at the Si samples was attenuated by neutral density filters so that low-level injection (~10^{-6} mW cm^{-2}) conditions were maintained. The photoconductivity responses were invariant to small changes to illumination intensities.

Table S1. Measured[a,b] Lifetimes, τ, and Surface Recombination Values, *S*, of CH_3-Terminated n-Si(111) Substrates After Processing Steps

	As-prepared		Au NP solution soak		Heat 230 °C	
Sample # [c]	**τ /μS**	***S* /cm s^{-1}**	**τ /μS**	***S* /cm s^{-1}**	**τ /μS**	***S* /cm s^{-1}**
1	442	55.4	483	50.7	586	41.8
2	589	41.6	584	42.0	557	44.0
3	581	42.2	755	32.4	819	29.9
4, control[d]	588	41.7	594	41.2	641	38.2
average	550 ± 70	45 ± 7	600 ± 140	42 ± 9	650 ± 140	39 ± 8

a. Low-level injection at ~ 1 x 10^{-6} mW cm^{-2}

b. λ = 828.7 ± 0.6 nm

c. Float Zone-grade Si, R = 4-6 kΩ cm, d = 490 μm

d. CH_3-terminated Si(111) that had not been further processed or treated

S7. X-ray Photoelectron Spectroscopy

Spectra were obtained on n-Si(111) with a resistivity of 1-8 Ω cm (Virginia Semiconductor Inc). Samples were diced into 1 cm x 1 cm squares and chemically modified as in S2. Samples were treated as described in S5 and immediately loaded into the x-ray photoelectron spectrometer. Spectra were obtained using an MProbe XPS employing a 1486.6 eV Al Kα X-ray source. Emitted photoelectrons were collected at θ=35° from the sample surface and the pressure was kept ≤ 1 x 10^{-8} torr during measurements. The measured photoelectron kinetic energies are referenced to the Fermi level of the spectrometer and are reported as binding energies (eV). High resolution Si 2p spectra were collected between 97 and 107 eV, with a spectrometer resolution of ~ 0.8 eV. Analyzed and reported spectra were averaged over 150 scans.

Estimation of surface oxide thicknesses, *d*, was performed assuming a substrate-overlayer model[6] (eq (S1)):

$$d = \lambda_{ov} \sin\theta \left[\ln\left(1 + \left(\frac{I_{Si}^{0}}{I_{ov}^{0}} \right) \left(\frac{I_{ov}}{I_{Si}} \right) \right) \right] \qquad \text{(S2)}$$

where λ_{ov} is the attenuation factor through the oxide layer, the term $\frac{I_{Si}^{0}}{I_{ov}^{0}}$ is an instrumental normalization factor for signals generated by pure Si vs. pure SiO_2, I_{Si} is the integrated intensity measured between 99 and 101 eV (for the bulk Si $2p_{3/2}$ and Si $2p_{1/2}$ signatures), and I_{ov} is the integrated signal intensity collected between 101 and 107 eV. The values for λ_{ov} and $\frac{I_{Si}^{0}}{I_{ov}^{0}}$ were taken as 2.6 nm and 1.3, respectively.[6,7]

S8. Long Term Photostability

The *J-V* properties of the CH_3-terminated Si/Au NP devices under illumination were tested as a function of age. For all devices, a slight decrease of 10 - 20 mV in the recorded V_{oc} values was observed after aging approximately 1 month in ambient conditions. A typical degradation of the photoresponse in such a device is highlighted in Figure S2.

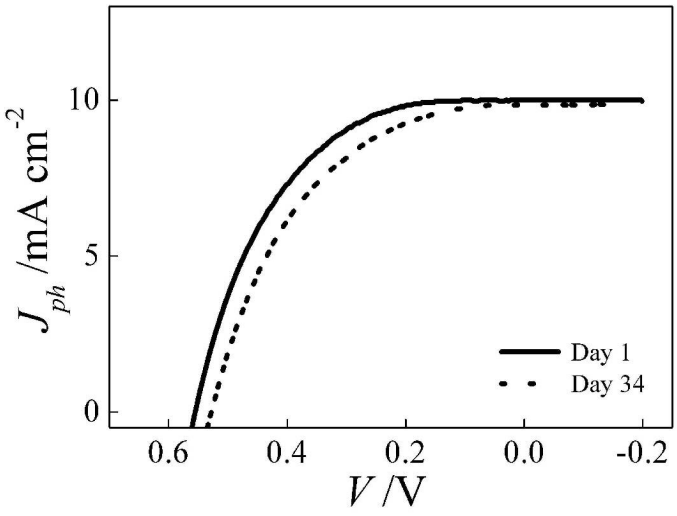

Figure S2. The time dependence of the current density vs. voltage responses for a n-Si/Au device made with a sintered Au NP film and CH_3-terminated Si(111) on (solid line) day 1 and (dashed line) day 34. The illumination intensities were maintained to generate short circuit current densities of 10 mA cm^{-2}. The device was kept in a plastic box to protect from dust but was otherwise subject to ambient conditions.

S9. References

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